NUCLEAR MAGNETIC RESONANCE STUDY OF THE TRIFLUOROVINYL GROUP

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ACKNOWLEDGMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure   Page

HISTORICAL BACKGROUND

Since about 1950, a great deal of work has been
undertaken in order to explain the nature of F^{19} chemical
shifts and F^{19} - F^{19} coupling constants. Although the
theoretical work has been limited and the experimental
results ambiguous at times, some advancements have been
made.

The chemical shift is caused by a magnetic shielding
of the nucleus due to the electron distribution about the
nucleus of interest. It consists of two terms: 1) Lamb's
(1) diamagnetic correction related directly to the electron
density at the nucleus, and 2) a paramagnetic term arising
from lack of spherical symmetry of the potential of the
electrons in the vicinity of the nucleus. Saika and
Slichter (2) devised a procedure for calculating the second-
order paramagnetic terms and were able to calculate the
shift between HF and F_2. According to their theory,
variations in the local paramagnetic circulations of the
fluorine atom are the dominant cause of chemical shifts in
fluorine compounds. This paramagnetic contribution, which
represents a shift toward low field, is greatest in co-
valently bonded fluorine and is zero in the spherically
symmetric F^- ion. Based on this theory, the magnitude of

the paramagnetic contribution may thus be expected to depend on the amount of ionic character in the chemical bond.

A series of binary covalent compounds was examined by Gutowsky and Hoffman (3,4) in an attempt to determine the effect of the electronic structure associated with bond formation and of the electronic configuration of the other atoms in the molecule. The results showed a decrease of the nuclear magnetic shielding of the F^{19} nucleus with increased electronegativity of the adjacent atom. This implies that the more tightly electrons are held by the atom bound to fluorine, the less effective the electrons are in magnetically shielding the fluorine nucleus.

Fluorine magnetic resonance shifts have been measured in the halomethanes (5). In the series CFH_3, CF_2H_2, CF_3H and CF_4 there is a progressive displacement of the fluorine chemical shifts to lower fields. Thus the effective group electronegativity influencing the fluorine in each compound may be expected to increase in the order $-CH_3 < -CH_2F < -CHF_2 < -CF_3$. This, of course, is further support of the general correlation of fluorine chemical shifts with electronegativity of the atom or group of atoms to which the fluorine is bonded. One would expect a similar trend of the fluorine shifts in the series $CFCl_3$, CF_2Cl_2, CF_3Cl and CF_4. However, the observed chemical shifts are in the opposite direction. Gutowsky (5) has proposed that, because of the

greater tendency of fluorine to form partial double bonds as compared with chlorine, the F atom should be less shielded as the number of chlorine atoms goes from zero to three.

Fluorine chemical shifts for a number of fluorocarbons and fluorocarbon derivatives have also been measured (6,7). Two important trends found are: 1) the progressive displacement of F resonance to lower field in series CF, CF_2 and CF_3 and 2) the shift to lower field of the CF_2 group fluorine resonance as the electronegativity of the directly attached substituent decreases. The first trend suggests that the amount of charge which fluorine is able to draw from a carbon decreases as the number of competing fluorines bonded to carbon increase. From his measurements of several perfluoroalkyl halides, Tiers (7) has postulated a "repulsive unshielding" effect to account for the second trend. The bulkiness of groups such as CCl_3 and I was considered to give rise to steric interactions which compensate for the lesser electronegativity in withdrawing electrons from a neighboring CF_2 group. Smith and Smith (8) have studied the fluorine shifts of some chlorofluorocarbons and have also observed the shift to lower fields of the fluorine resonance as the total electronegativity of the atoms associated with the nearest carbon atom decreases. A covalent bond or double-bond mechanism was given by them as an explanation of the observed change in the chemical shift values.

Investigations by Gutowsky, McCall, McGarvey and Meyer (9) on the substituent effects in some fluorobenzene derivatives led to an apparent direct relation between the Hammett substituent constant and the nuclear shielding for the fluorine nucleus attached to the benzene ring.

The theory of indirect nuclear spin-spin interactions is based upon the complete Hamiltonian for the electron nuclear interactions as was first outlined by Ramsey and Purcell (10), and later developed in more detail by Ramsey (11). There are three principal terms in the Hamiltonian which contribute to spin-spin coupling. They are an orbital term, a dipole-dipole term, and a Fermi term. These three terms represent the interaction of the nuclear magnetic moments with the electron orbital motion and with the electron spin density at a distance from, and at, the nucleus (12).

Physically, spin-spin coupling between nuclei arises because of the magnetic interaction of each nucleus with the spin or orbital angular momentum of a "local" electron, together with the coupling of electron spins and/or orbital angular momenta with each other. In short, the nuclear interactions proceed via the electronic structure of the molecule.

The problem of the theoretical calculation of coupling constants between protons has been considered by several

authors (13,14,15). It has been demonstrated that for the
coupling between protons only the Fermi contact term
contributes appreciably, and the magnetic dipolar and
electron-orbital interaction may be neglected. It is now
generally believed that proton-proton spin coupling proceeds
through the electronic structure in the intervening bonds
(14). This "through-bond" mechanism is in line with the
common observation that the magnitude of the coupling
constants decreases with increasing number of bonds sepa-
rating the nuclei.

On the other hand, not much progress has been made
in the theoretical prediction of fluorine-fluorine coupling
constants, although a considerable number of such coupling
constants have been determined experimentally. The most
complete treatment of this problem is that of McConnell
(16) who applied molecular orbital theory to the evaluation
of the coupling in C_2F_4, and demonstrated that reasonable
values for coupling constants could be obtained by
considering contributions from magnetic dipolar and electron-
orbital terms. Karplus (17), on the other hand, has
suggested that electron-orbital and dipolar electron-spin
terms often may not be very important. However, even though
Karplus, McConnell and others may disagree on the exact
mechanism involved in fluorine-fluorine coupling, they do
agree that the problem of fluorine-fluorine coupling is

certainly more complicated than in the case of coupling between protons. This prediction was experimentally sub- stantiated in 1956, when Saika and Gutowsky (18) reported a near zero coupling constant between the fluorine atoms on adjacent carbon atoms in the molecule $CF_3CF_2N(CF_3)_2$. This was particularly surprising, since the other two constants are 16 cycles per sec (cps) and 6 cps for fluorine nuclei separated by four and five bonds, respectively.

Since that time similar cases for near-zero coupling between vicinal fluorines in the CF_3CF_2 group have been reported in the literature (19,20,21). Crapo and Sederholm (19) first postulated that the near-zero coupling constants come about as a result of averaging non-zero coupling constants over the three stable configurations with respect to rotation about the connecting carbon-carbon bond. Subsequently, Petrakis and Sederholm (22) have shown this idea to be non-valid, since such accidental averaging would lead one to predict that the coupling constants between vicinal fluorine in all compounds having the CF_3CF_2 group would be nearly zero, which is not the case. They concluded that the coupling constants between fluorine atoms in saturated organic compounds can be explained if one assumes that coupling takes place primarily directly through space rather than through the bond. According to this "through- space" mechanism, fluorine atom coupling is almost completely

due to direct overlap of orbitals on the two fluorine atoms. Sederholm and Petrakis further postulated that coupling constants become zero when the distance between fluorine atoms become greater than 2.72Å, approximately twice the Van der Waals radius for the fluorine atom. In the CF_3CF_2 group the calculated internuclear distance between two fluorine atoms on adjacent carbons is greater than 2.72Å.

However, if one considers the F—C—C—F coupling constants in a substituted ethane, it is apparent that if the trans constant is as great as that for the gauche relationship, the major part of the coupling could not be transmitted through space. For example, the trans coupling constant for $CF_2BrCFBr_2$ (23) is 16.2 cps and the gauche coupling constant is 18.6 cps. Also, if one considers the system CF_3-CFXY, one finds results for the F—C—C—F constants as follows: CF_3CH_2F (24) 15.6 cps, and CF_3-$CFCl_2$ (25) 5.7 cps. These results are certainly not easily explained if one agrees that the "through-space" mechanism is the only mechanism for vicinal fluorine-fluorine coupling.

Recently, Ng and Sederholm (26) have explained the above mentioned results on the basis of two fluorine-fluorine spin coupling mechanisms; the "through-bond" and the "through-space" mechanisms. The "through-bond" mechanism proceeds through the electronic structure in the intervening bonds, as is the case with proton coupling, whereas the

"through-space" mechanism becomes operative only when there is direct overlapping of the electronic clouds of the fluorine atoms. They postulated that in the case of vicinal fluorines only the "through-bond" mechanism is important and that the magnitude of the "through-bond" coupling is governed by the electron withdrawing power of the other substituents attached to carbon skeleton which can cause the coupling to vanish. When fluorine nuclei are separated by more than three bonds, the coupling, though diminishingly small from the "through-bond" mechanism, may be enhanced if the geometry of the molecule allows the nuclei to get into close proximity so that the "through-space" mechanism becomes operative.

It is generally agreed that fluorine-fluorine couplings do proceed by more than one mechanism. Now, the principal problem that is to be solved is the relative extent to which fluorine-fluorine couplings are transmitted by overlap of the p electrons of one fluorine atom with another fluorine atom not directly bonded to the first, or alternately, by polarization of the electrons occupying the intervening bond orbitals.

In addition to unravelling the subtle nature of fluorine-fluorine coupling constants, there are as yet many other problems concerning fluorine-fluorine couplings in fluorocarbons and fluorocarbon derivatives which remain to

be investigated. Two such problems are the effect of different substituents and the effect of temperature on the fluorine-fluorine coupling constants in certain fluorocarbon derivatives. The object of such investigations would be to lend insight into the effect of molecular geometry and molecular motion on the coupling constants and chemical shifts.

The dependence of nuclear spin-spin coupling constants upon molecular geometry is of considerable interest and importance. The theoretical work of Gutowsky, Karplus, and Grant (15) on the angular dependence of electron coupled proton interactions in the CH_2 group has led to calculated results which are in general agreement with experimental results. The results were calculated from a valence bond treatment and were made for static molecules in their equilibrium configuration. They showed that the geminal coupling constants decrease with increasing H—C—H' angle.

Gutowsky, Mochel, and Somers (27) have further postulated that because the predicted angular dependence of the coupling is nonlinear, the bond-bending vibrations should give an average for the H—H and H—F coupling constants in the CH_2 and CHF groups, respectively, which is appreciably larger than that for the corresponding equilibrium, but static, angle. The detection of this averaging effect requires that the vibrational amplitudes be modified. Gutowsky (27)

suggests that this may be accomplished either by changing the temperature of a sample or by isotopic substitution. Several isotope effects upon chemical shifts have been observed in the high-resolution nuclear magnetic resonance spectra of H^1 and F^{19} nuclei (28,29,30,31,32,33). Such observations led to the suggestion (27) that the difference in vibrational amplitudes is the primary cause of the isotope chemical shifts, and that there might also be observable vibrational effects upon electron coupled nuclear spin-spin interaction.

Petrakis and Sederholm (22) have found that chemical shifts of various gaseous compounds vary with temperature. This effect was ascribed to excitation of vibrational modes of the molecules, the protons in the excited molecules being differently shielded than the protons in the ground vibrational state. Schug, McMahon and Gutowsky (34) have done theoretical calculations for the temperature dependence of the proton-proton coupling in substituted ethanes. They found that torsional vibrations produce a slight temperature dependence of opposite sign for the trans and gauche coupling. However, for molecules in which the potential function has threefold symmetry, rotational averaging leads to a cancellation of the vibrational effects, giving a temperature independent value for the average coupling. This prediction was experimentally verified on

ethyl nitrate for which the proton-proton coupling constant
was found to be invariant over a 100° temperature range.

Gutowsky, Belford and McMahon (35) have observed the
H^1 and F^{19} magnetic resonance spectra of several poly-
substituted ethanes over temperature ranges of 250° to
450°K. By assuming that the temperature dependence of the
chemical shifts and coupling constants results only from a
change in the equilibrium concentration of the rotamers,
they were able to calculate the relative energies of the
different rotamers. Similar investigations using the above
assumptions, have been done by Fessenden and Waugh (36) and
Abraham and Bernstein (37).

A second method of calculating the potential energy
as a function of internal rotation in substituted ethanes
was proposed by Thompson, Newmark and Sederholm (38). They
utilized the Boltzmann energy distribution to calculate the
free energy associated with the various rotamers from their
integrated areas as obtained from the fluorine magnetic
resonance spectra at various temperatures.

Most of the work in the literature dealing with the
effects of substituents on fluorine-fluorine coupling
constants in fluorocarbon derivatives is concerned with the
dependence of the coupling constants on the electro-
negativity of the substituents attached to the carbon
skeleton. Dyer (39) has shown that the fluorine geminal

coupling constants in substituted ethanes vary widely in
magnitude and are dependent on the electronegativity of the
third substituent attached to the carbon atom. Ng and
Sederholm (26) have reported that the vicinal coupling
constants in a series of halogen substituted ethanes and
propanes are inversely proportional to the sum of the
Pauling electronegativities of the substituents. This,
they say, suggests that highly electronegative substituents
withdraw the excited triplet or π state electrons, which
are responsible for the transmission of nuclear spin
information, from the bonds between the interacting nuclei,
thereby reducing the coupling constants.

INTRODUCTION

In order to undertake a study of any fluorocarbon
derivatives, such as the trifluorovinyl derivatives, one
must take into consideration fluorine chemical shifts and
fluorine spin-spin coupling constants. As yet, the
theoretical work that has been done on these two NMR
parameters is limited and, therefore, some of the experi-
mental results are ambiguous. However, a great deal of the
experimental work done on both parameters has, in some
instances, led to important information concerning the
nature of the F^{19} chemical shifts and the F^{19} - F^{19} coupling
constants. Also, the experimental work done on substituent
effects and temperature-dependent effects show much promise
with regard to molecular geometry and molecular motions.

Much of the earlier work (40,41,42) related to the
trifluorovinyl group has been very limited. The only
conclusion that can be drawn from this earlier work is that
the chemical shifts and coupling constants of the three
fluorine atoms are quite sensitive to the nature of the
substituent to which the trifluorovinyl group is attached.
As yet, no correlations have been made between the two NMR
parameters and substituent effects. The only temperature
dependent work done on any trifluorovinyl derivatives was

carried on by Ramey and Brey (43). This work was limited to perfluoropropenyl halides.

The primary purpose of the present investigation was twofold: 1) to determine experimentally the effect of substituents upon the F^{19} chemical shifts and $F^{19} - F^{19}$ coupling constants within the trifluorovinyl group, and 2) to determine the effect of temperature change upon $F^{19} - F^{19}$ coupling constants.

The secondary purpose was to attempt to relate the observed changes to the mechanism of transmission of spin-spin coupling and to changes in molecular conformation.

EXPERIMENTAL AND EXPERIMENTAL RESULTS

Experimental

The spectra were obtained with a Varian spectrometer operating at 56.4 mc./sec. Audio-frequency modulation of the magnetic field was used to produce sidebands, the frequency of which was continuously monitored by a Hewlett-Packard 523B frequency counter. From eight to ten replications of the spectrum were graphically recorded, and the frequency separations were calculated from the averaged distances measured from the chart paper. Chemical shifts were obtained by substituting a tube of trifluoroacetic acid in the probe while sweeping the field continuously through the resonances of the reference and of the sample.

The temperature of the sample was regulated by adjusting the flow rate of dry nitrogen passing through a Varian V 4340 variable temperature probe assembly. For the low-temperature measurements, the nitrogen was cooled by passing it through a copper coil immersed in liquid nitrogen. A copper-constantan thermocouple placed within the Dewar insert was used to determine the temperature, which was considered accurate to within $\pm$ 2°.

The difficulties encountered in obtaining a homo-geneous field at the lower temperatures were overcome by

15

the use of a standard sample. An olefin exhibiting promi-
nent fine structure was used to adjust the field.

The silanes studied in this investigation were
prepared by W. H. Oliver of this department, and the fluoro-
propenes by Dr. J. Savory (44). The remaining trifluorovinyl
derivatives were prepared by Dr. D. Sayers of this department
and by the research division of Peninsular Chemresearch,
Inc., Gainesville, Florida.

Experimental Results

From a consideration of the generalizations as
derived from previous work (40,41,42) on the nuclear spin-
spin coupling constants in fluorolefins, it is possible to
assign unambiguously the multiplets corresponding to the
various nuclei. These generalizations are: 1) J_{trans}
is much larger than J_{cis} in all reported cases; 2) J_{gem}
is usually larger than J_{cis} but less than J_{trans}, and 3)
the chemical shift of F_x in the molecule $F_aF_bC=CF_x$, is at
higher field than those of F_a and F_b. All the compounds
studied have first-order spectra so that the coupling
constants may be obtained directly from multiplet sepa-
rations.

In Tables 1 and 2 are given the chemical shifts and
coupling constants within the trifluorovinyl group for the
several compounds as neat liquids at room temperature. The

TABLE 1

CHEMICAL SHIFTS AND COUPLING CONSTANTS WITHIN THE TRIFLUOROVINYL GROUP AT 32°C FOR COMPOUNDS IN GROUPS I AND II

$$F_a\!\!-\!\!C = C\!\!-\!\!F_x, \quad F_b, \quad Y$$

Y	Chemical shifts, ppm from CF_3COOH			Coupling constants, cps		
	F_a	F_b	F_x	J_{ab}	J_{ax}	J_{bx}
Group I						
$-(CH_2)_2Br$	26.9	45.7	100	84.8	32.9	113.7
$-(CH_2)_4CF\!=\!CF_2$	30.4	49.5	96.8	91.4	32.5	113.8
$-(CH_2)_2Si(CH_3)_3$	30.1	48.2	97.5	92.5	31.9	113.9
$-(CH_2)_3Si(CH_3)_3$	28.5	40.2	97.4	90.9	32.3	114.0
$-Cl*$	25	41	65	78	58	115
$-Br*$	-	-	-	75	57	124
$-H*$	23	47	105	87	33	119
Group II						
$-OCF_3$	40.8	48.5	62.8	87.5	65.1	111.0
$-OCH_2CF_3$	46.6	52.9	62.7	101.6	57.8	106.8

*Values for the chemical shifts and coupling constants are approximate and were obtained from reference 42.

TABLE 2

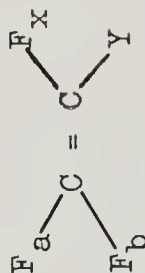### CHEMICAL SHIFTS AND COUPLING CONSTANTS WITHIN THE TRIFLUOROVINYL GROUP AT 32°C FOR COMPOUNDS IN GROUP III

$$F_a \diagdown C = C \diagup F_x$$
$$F_b \diagup \diagdown Y$$

Y	Chemical shifts, ppm from CF_3COOH			Coupling constants, cps		
	F_a	F_b	F_x	J_{ab}	J_{ax}	J_{bx}
Group III						
$-B(CF_2=CF_2)_2$*	-7.3	11.1	107	5	24	110
$-COF$	0.6	12.3	110	6.6	36.8	114.4
$-CN$	3.2	26.6	114	28.4	35.2	117
$-SCF_3$	6.9	25.6	76.5	30.4	41.7	122.3
$-I$	10.3	35.5	71.8	65.3	52.2	127
$-Si(CH_3)_3$	11.3	40.2	122	71.6	25.9	116.8
$-Si(CH_3)_2H$	10.3	39.7	122	68.3	25.6	117.5
$-Si(CH_3)_2OC_2H_5$	11.4	38.9	123	67.2	25.6	117
$-Si(CH_3)_2C_6F_5$	8.6	36.8	122	64.2	24.6	117.5
$-Si(CH_3)_2Cl$	7.8	34.6	122	60.5	25.5	117.8
$-CF_3$	19.0	32.3	119	57.5	39.4	118
$-CF_2Cl$	19.5	30.2	108	57.0	39.0	116
$-CF_2Br$	18.8	28.9	105	54.7	38.0	115
$-CF_2I$	18.5	27.6	98	53.4	36.2	115

*Values for the chemical shifts and coupling constants are approximate and were obtained from reference 42.

18

several compounds have been divided into three groups for
a particular reason which will be explained later. Room
temperature values for the geminal coupling constants, J_{ab},
and the values for the chemical shift of F_a for the various
compounds are plotted in Figure 1.

In Table 3 are listed the room temperature values
for the cis coupling constant, J_{ax}, the values for the
chemical shift of F_x, and the Pauling electronegativity of
the substituent atom directly attached to the trifluorovinyl
group. J_{ax} and the chemical shifts of F_x are plotted
against electronegativity values in Figures 2 and 3,
respectively.

Values for the cis coupling constants, J_{ax}, and J_{ab}
over a range of temperatures are listed in Tables 4 through
9 and are plotted in Figures 4 through 9. The changes of
the values with temperature are usually fairly small; how-
ever, they seem clearly to be significant.

Values for the trans coupling constants, J_{bx}, over
a range of temperatures are listed in Tables 10 through 12
and are plotted in Figures 10 through 12. The trans
coupling constant appears to be insensitive to temperature
change in all compounds studied.
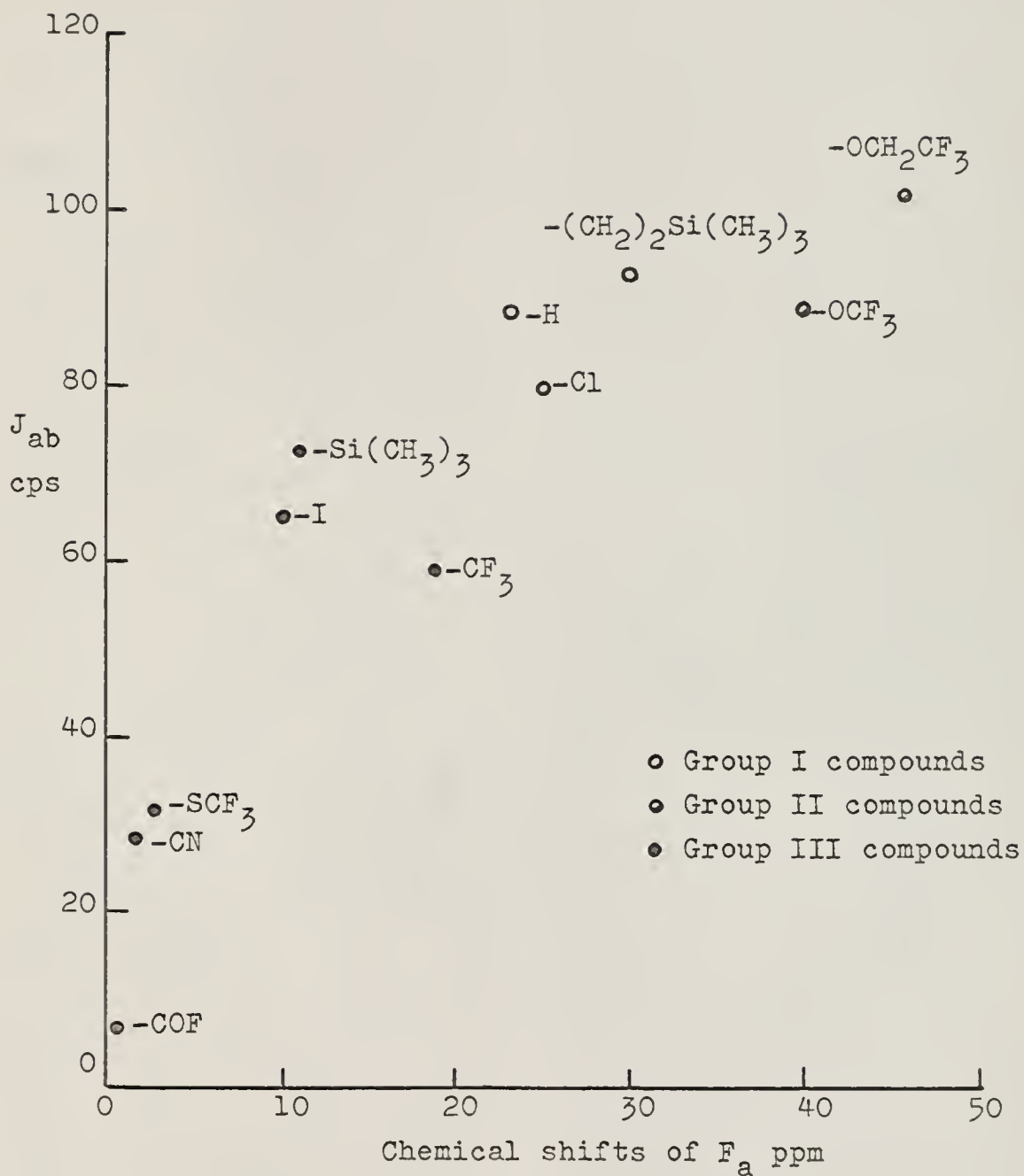
Fig. 1.-The correlation between J_{ab} and the chemical shifts of F_a observed in some of the tri-fluorovinyl compounds.

TABLE 3

CORRELATION OF J_{ax} AND THE CHEMICAL SHIFTS OF F_x WITH THE
ELECTRONEGATIVITY OF THE SUBSTITUENT ATOMS

Substituent atom	Pauling* electronegativity	J_{ax}, cps	Chemical shift of F_x, ppm
Si	1.8	25.4**	122*
B	2.0	24	107
H	2.1	33	105
C	2.5	35.3**	105**
S	2.5	41.7	76.5
I	2.5	52.2	71.8
Br	2.8	57	--
Cl	3.0	58	65
O	3.5	61.5**	62.8**

*Values obtained from reference 45.

**Average values obtained from values for those compounds containing the same substituent atom listed in Tables 1 and 2.
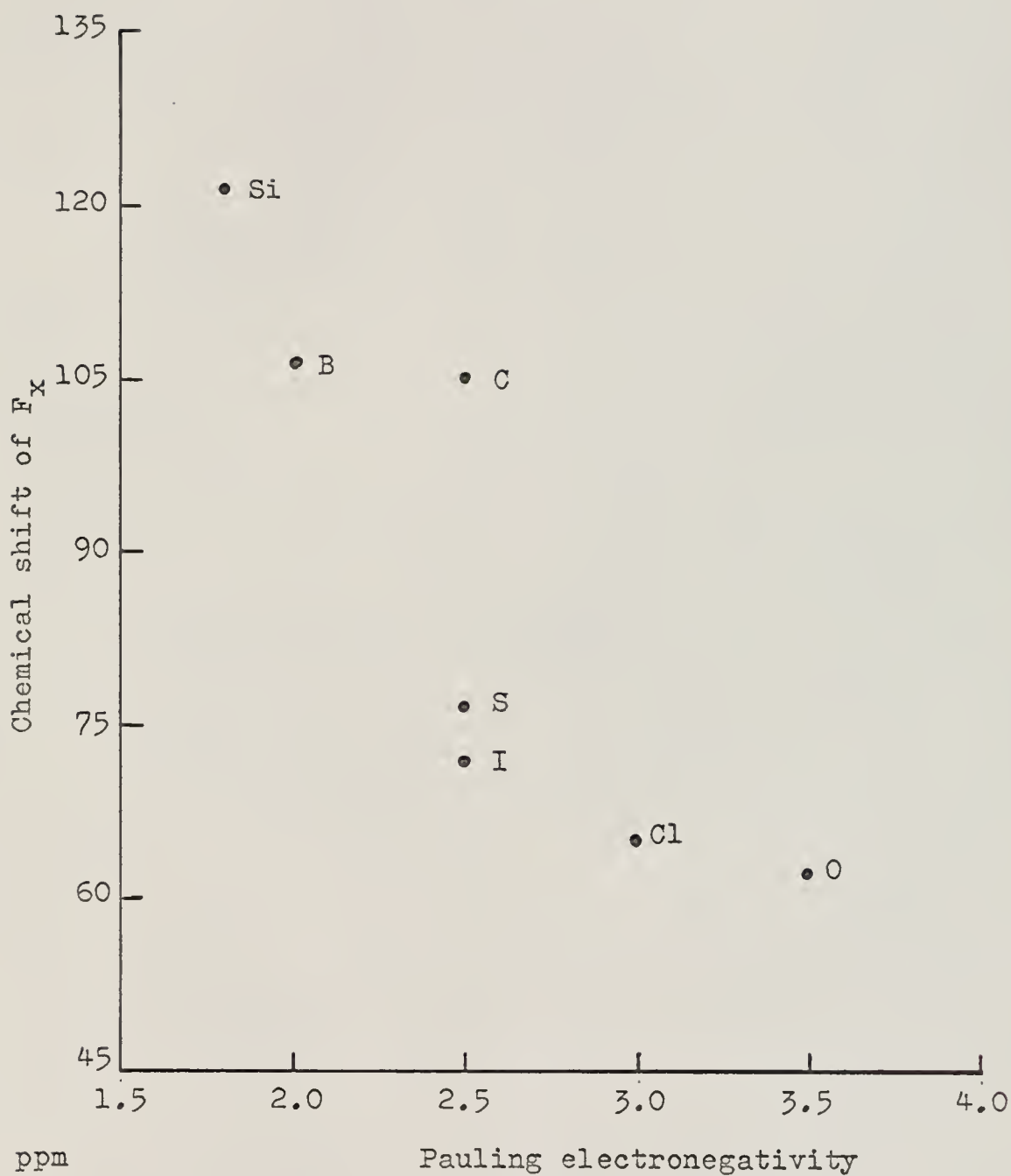
Fig. 2.-The correlation between the chemical shifts of F_x and the electronegativity of the substituent atoms observed in some of the trifluorovinyl compounds.
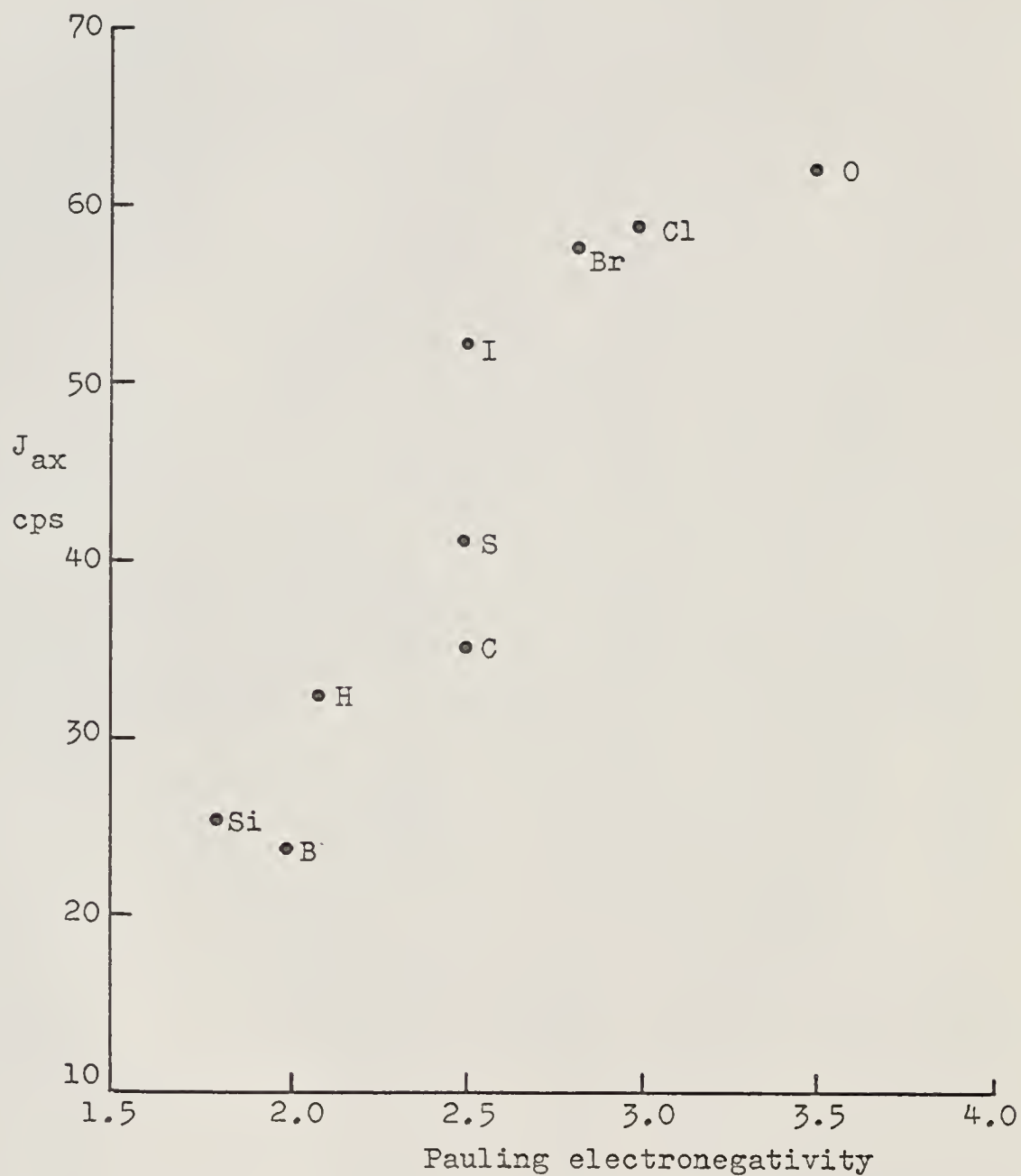
Fig. 3.-The correlation between J_{ax} and the electronegativity of the substituent atoms observed in some of the trifluorovinyl compounds.

TABLE 4

THE TEMPERATURE DEPENDENCE OF J_{ab} OBSERVED IN SOME
TRIFLUOROVINYL COMPOUNDS OF GROUP I

$$\begin{array}{c} F_a \\ \diagdown \\ \diagup \\ F_b \end{array} C = C \begin{array}{c} \diagup F_x \\ \\ \diagdown Y \end{array}$$
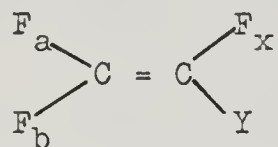
Y = $-(CH_2)_2Br$		Y = $-(CH_2)_2CF=CF_2$		Y = $-(CH_2)_2Si(CH_3)_3$	
Temp. °C	J_{ab}	Temp. °C	J_{ab}	Temp. °C	J_{ab}
86	85.0 ± 0.1	32	91.4 ± 0.1	82	93.1 ± 0.2
55	84.7 ± 0.2	-19	91.2 ± 0.2	60	92.8 ± 0.2
32	84.8 ± 0.2	-52	91.1 ± 0.1	32	92.5 ± 0.1
-10	84.6 ± 0.2	-90	91.0 ± 0.3	-38	92.1 ± 0.2
-55	84.5 ± 0.1	-105	91.0 ± 0.3	-78	91.8 ± 0.2

TABLE 5

THE TEMPERATURE DEPENDENCE OF J_{ab} OBSERVED IN SOME
TRIFLUOROVINYL COMPOUNDS OF GROUP II

$$\begin{matrix} F_a \\ \end{matrix} C = C \begin{matrix} F_x \\ Y \end{matrix}$$

$$F_b$$
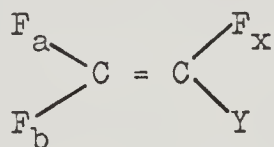
Y = $-OCF_3$		Y = $-OCH_2CF_3$	
Temp. °C	J_{ab}	Temp. °C	J_{ab}
32	87.5 ± 0.1	32	101.6 ± 0.1
-10	87.0 ± 0.1	-10	101.3 ± 0.2
-28	86.7 ± 0.1	-30	100.9 ± 0.1
-63	86.4 ± 0.2	-72	100.6 + 0.2
-105	85.7 ± 0.2	-115	100.1 ± 0.2

TABLE 6

THE TEMPERATURE DEPENDENCE OF J_{ab} OBSERVED IN SOME

TRIFLUOROVINYL COMPOUNDS OF GROUP III

$$F_a \diagdown C = C \diagup ^{F_x}_{Y}$$
$$F_b \diagup$$
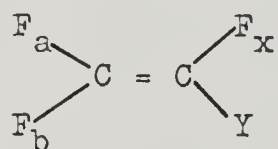
Y = $-SCF_3$		Y = $-Si(CH_3)_2H$		Y = $-Si(CH_3)_3$	
Temp. °C	J_{ab}	Temp. °C	J_{ab}	Temp. °C	J_{ab}
32	30.4 ± 0.1	55	69.0 ± 0.2	86	72.0 ± 0.1
-3	29.7 ± 0.1	32	68.3 ± 0.1	57	71.8 ± 0.1
-25	29.3 ± 0.1	-10	68.0 ± 0.1	32	71.6 ± 0.1
-65	28.5 ± 0.1	-55	67.7 ± 0.2	-33	70.8 ± 0.2
-105	28.1 ± 0.1	-92	67.0 ± 0.2	-97	70.1 ± 0.1

TABLE 7

THE TEMPERATURE DEPENDENCE OF J_{ax} OBSERVED IN SOME

TRIFLUOROVINYL COMPOUNDS OF GROUP I

$$\underset{F_b}{\overset{F_a}{>}} C = C \underset{Y}{\overset{F_x}{<}}$$
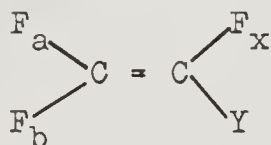
Y = $-(CH_2)_2Br$		Y = $-(CH_2)_2CF=CF_2$		Y = $-(CH_2)_2Si(CH_3)_3$	
Temp. °C	J_{ax}	Temp. °C	J_{ax}	Temp. °C	J_{ax}
55	33.3 ± 0.0	32	32.5 ± 0.1	82	32.6 ± 0.1
32	32.9 ± 0.1	-19	31.9 ± 0.1	60	32.2 ± 0.1
-10	32.5 ± 0.1	-52	31.6 ± 0.2	32	31.9 ± 0.1
-55	31.8 ± 0.1	-90	30.6 ± 0.2	-38	30.9 ± 0.1
-98	30.9 ± 0.1			-70	30.1 ± 0.1
				-96	29.8 ± 0.2

TABLE 8

THE TEMPERATURE DEPENDENCE OF J_{ax} OBSERVED IN SOME
TRIFLUOROVINYL COMPOUNDS OF GROUP II
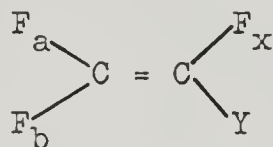
Y = $-OCF_3$		Y = $-OCH_2CF_3$	
Temp. °C	J_{ax}	Temp. °C	J_{ax}
32	65.1 ± 0.2	32	57.8 ± 0.0
-10	65.0 ± 0.0	10	57.6 ± 0.1
-28	64.8 ± 0.1	-30	57.5 ± 0.1
-63	64.7 ± 0.2	-52	57.3 ± 0.1
-105	64.4 ± 0.2	-72	57.2 ± 0.2
		-115	56.5 ± 0.1

TABLE 9

THE TEMPERATURE DEPENDENCE OF J_{ax} OBSERVED IN SOME

TRIFLUOROVINYL COMPOUNDS OF GROUP III

$$\begin{matrix} F_a & & F_x \\ & C = C & \\ F_b & & Y \end{matrix}$$
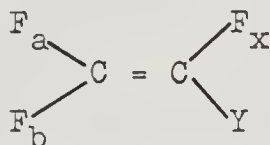
Y = $-SCF_3$		Y = $-Si(CH_3)_2H$		Y = $-Si(CH_3)_3$	
Temp. °C	J_{ax}	Temp. °C	J_{ax}	Temp. °C	J_{ax}
32	41.7 ± 0.2	55	25.8 ± 0.2	86	26.5 ± 0.1
-3	41.4 ± 0.1	32	25.6 ± 0.2	57	26.1 ± 0.1
-25	41.2 ± 0.1	-10	25.0 ± 0.1	32	25.9 ± 0.1
-65	40.8 ± 0.1	-55	24.6 ± 0.2	-33	24.8 ± 0.2
-105	40.2 ± 0.1	-92	23.8 ± 0.1	-97	23.9 ± 0.1

Fig. 4.—The temperature dependence of J_{ab} observed in some trifluoro-vinyl compounds of group I.

Fig. 5.—The temperature dependence of J_{ab} observed in some trifluoro-vinyl compounds of group II.
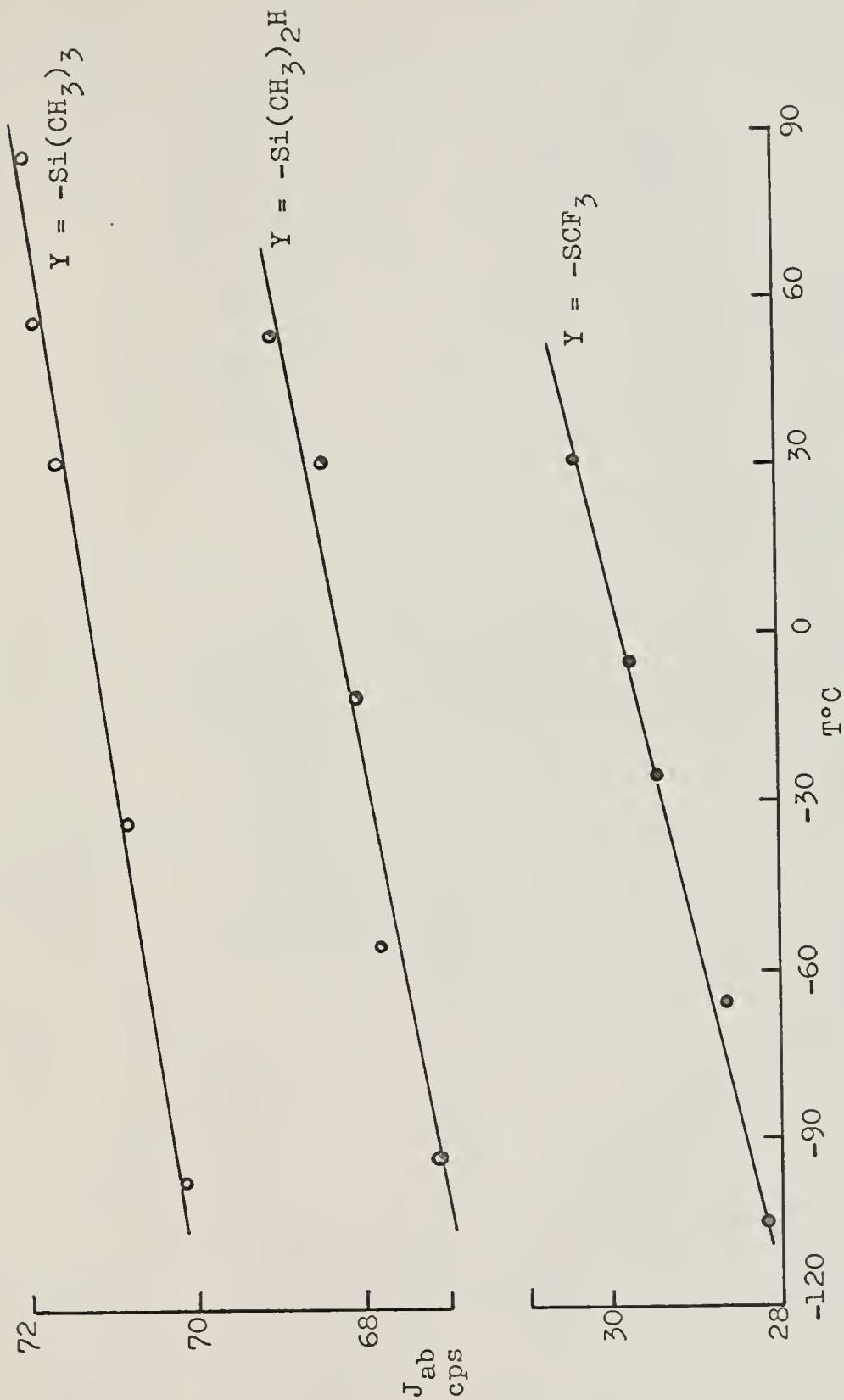
Fig. 6.—The temperature dependence of J_{ab} observed in some trifluoro-vinyl compounds of group III.
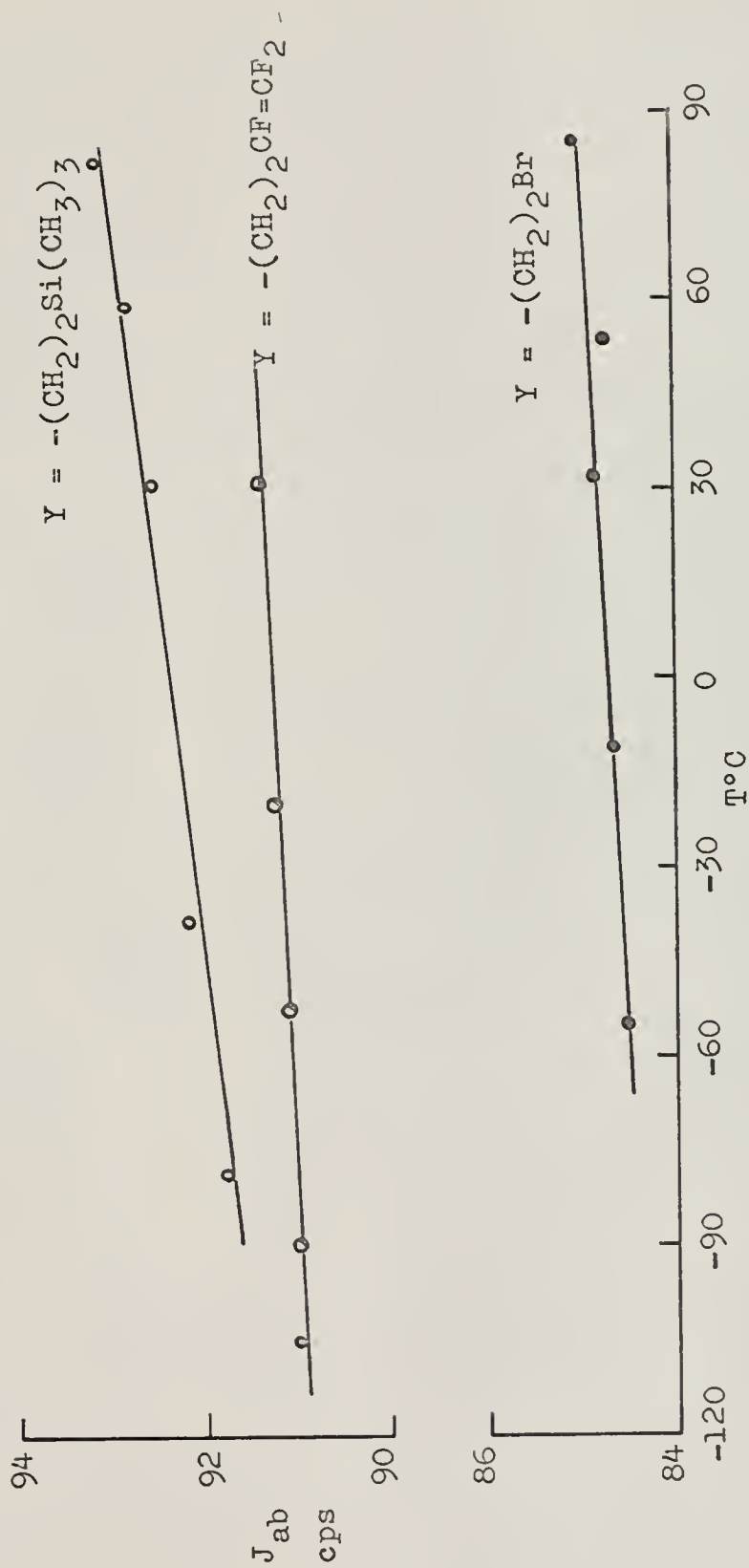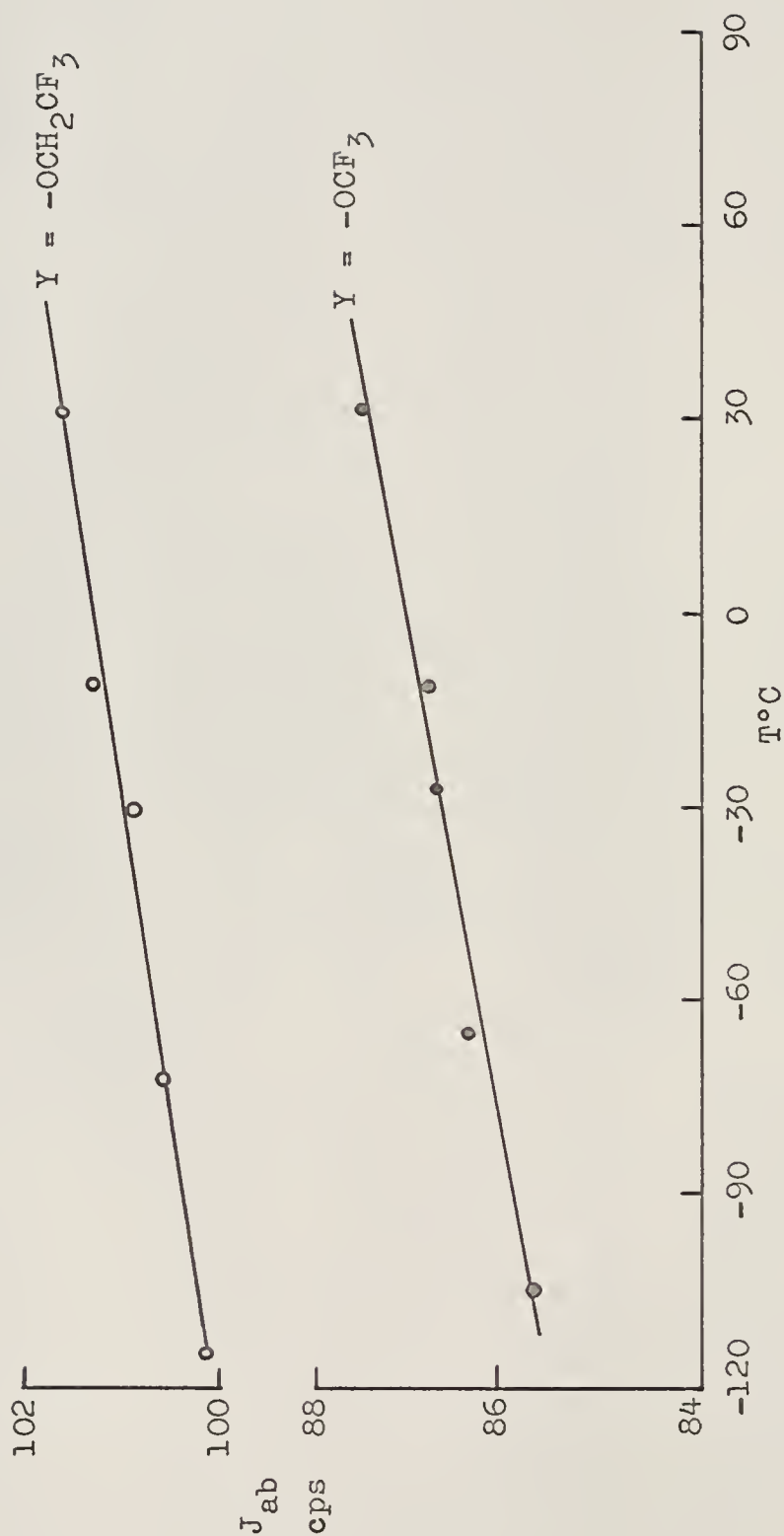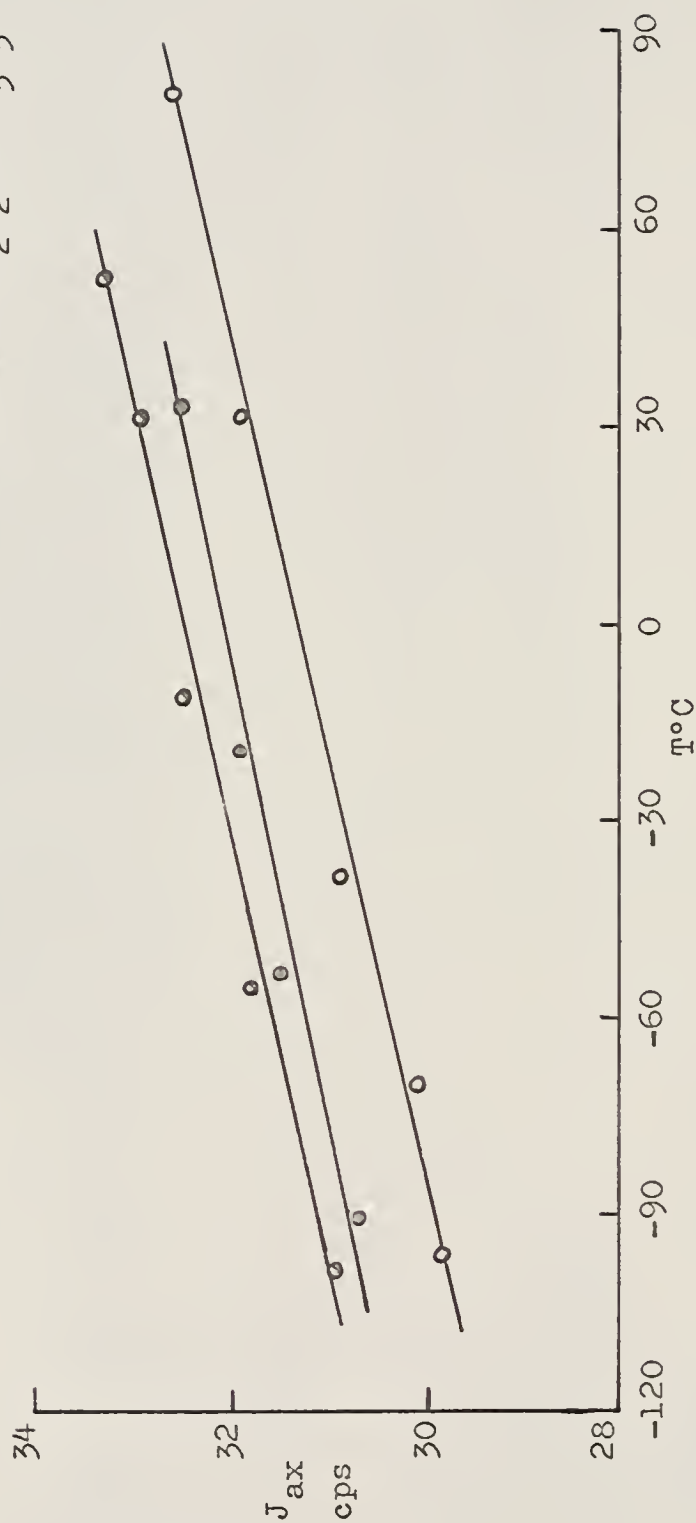
Fig. 7.—The temperature dependence of J_{ax} observed in some trifluoro-vinyl compounds of group I.

Fig. 8.—The temperature dependence of J_{ax} observed in some trifluoro-vinyl compounds of group II.

Fig. 9.—The temperature dependence of J_{ax} observed in some trifluoro-vinyl compounds of group III.

TABLE 10

THE TEMPERATURE DEPENDENCE OF J_{bx} OBSERVED IN SOME

TRIFLUOROVINYL COMPOUNDS OF GROUP I

$$\begin{array}{c} F_a \\ \diagdown \\ F_b \end{array} C = C \begin{array}{c} F_x \\ \diagup \\ \diagdown Y \end{array}$$
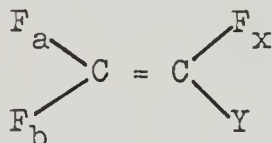
Y = -(CH$_2$)$_2$Br		Y = -(CH$_2$)$_2$CF=CF$_2$		Y = -(CH$_2$)$_2$Si(CH$_3$)$_3$	
Temp. °C	J_{bx}	Temp. °C	J_{bx}	Temp. °C	J_{bx}
32	113.7 ± 0.4	86	113.9 ± 0.2	82	113.8 ± 0.4
-19	113.8 ± 0.4	32	113.8 ± 0.4	32	113.9 ± 0.3
-52	113.6 ± 0.5	-10	114.0 ± 0.4	-38	113.9 ± 0.4
-90	113.7 ± 0.4	-55	113.8 ± 0.6	-70	113.8 ± 0.5
		-98	113.6 ± 0.6	-96	113.8 ± 0.7

TABLE 11

THE TEMPERATURE DEPENDENCE OF J_{bx} OBSERVED IN SOME

TRIFLUOROVINYL COMPOUNDS OF GROUP II

$$\begin{array}{c} F_a \\ \diagdown \\ F_b \end{array} C = C \begin{array}{c} F_x \\ \diagup \\ \diagdown \\ Y \end{array}$$
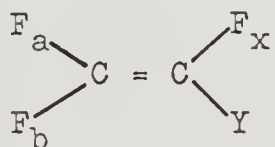
Y = $-OCF_3$		Y = $-OCH_2CF_3$	
Temp. °C	J_{bx}	Temp. °C	J_{bx}
32	111.0 ± 0.4	32	106.8 ± 0.4
-10	110.5 ± 0.6	10	106.4 ± 0.2
-28	110.5 ± 0.5	-30	106.4 ± 0.4
-63	111.0 ± 0.6	-72	106.2 ± 0.3
-105	111.5 ± 0.5	-115	106.6 ± 0.5

TABLE 12

THE TEMPERATURE DEPENDENCE OF J_{bx} OBSERVED IN SOME

TRIFLUOROVINYL COMPOUNDS OF GROUP III

$$\begin{array}{c} F_a \\ \diagdown \\ F_b \diagup \end{array} C = C \begin{array}{c} \diagup F_x \\ \diagdown Y \end{array}$$
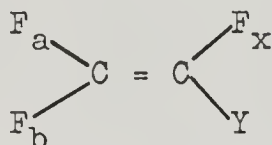
Y = $-SCF_3$		Y = $-Si(CH_3)_2H$		Y = $-Si(CH_3)_3$	
Temp. °C	J_{bx}	Temp. °C	J_{bx}	Temp. °C	J_{bx}
32	122.3 ± 0.4	55	117.4 ± 0.5	86	116.8 ± 0.4
-3	123.0 ± 0.4	32	117.5 ± 0.6	57	116.7 ± 0.4
-25	122.8 ± 0.4	-10	117.5 ± 0.6	32	117.0 ± 0.5
-65	123.0 ± 0.5	-55	117.5 ± 0.6	-33	117.0 ± 0.4
-105	123.0 ± 0.5	-92	117.4 ± 0.6	-97	116.6 ± 0.4
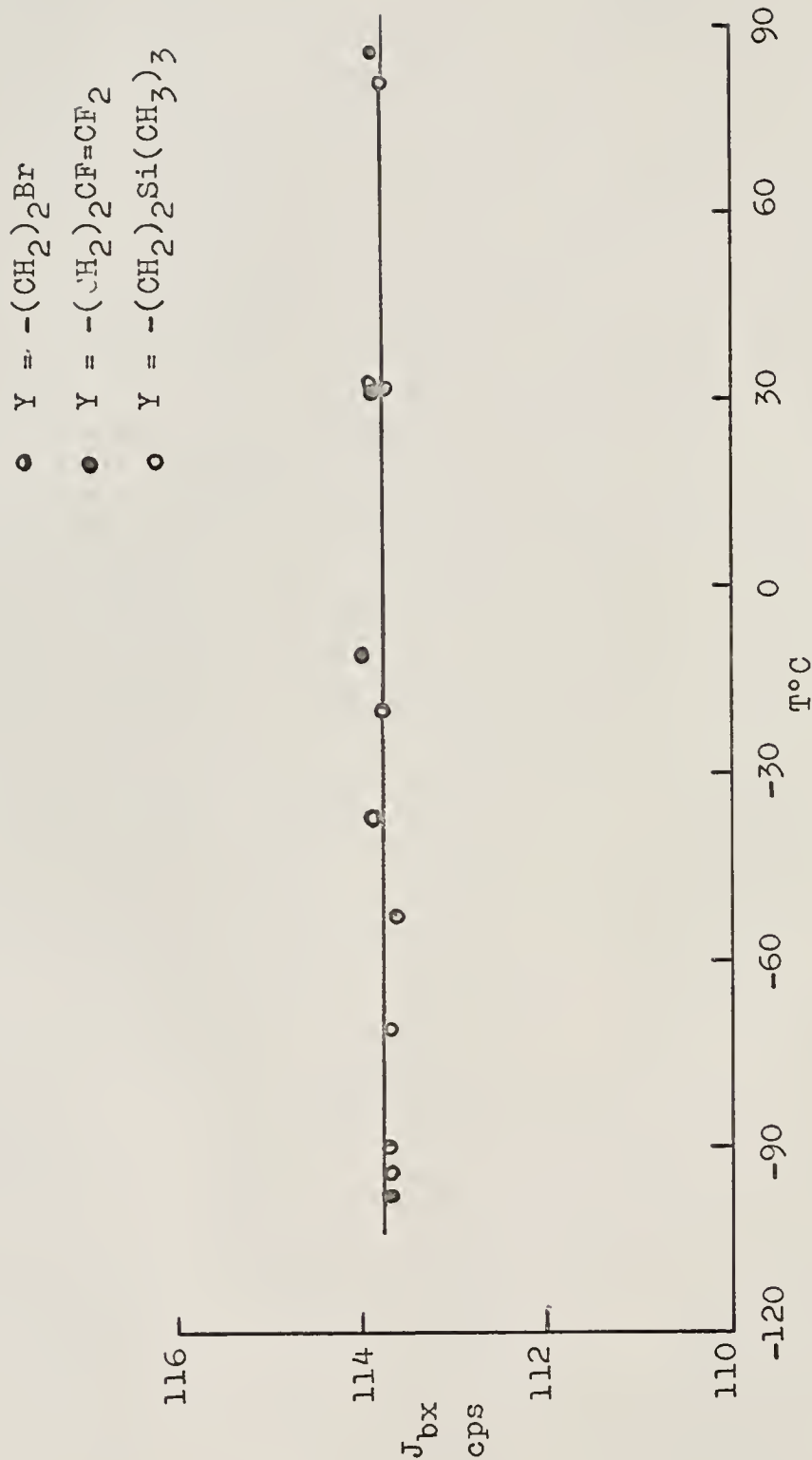
Fig. 10.—The temperature dependence of J_{bx} observed in some trifluoro-
vinyl compounds of group I.
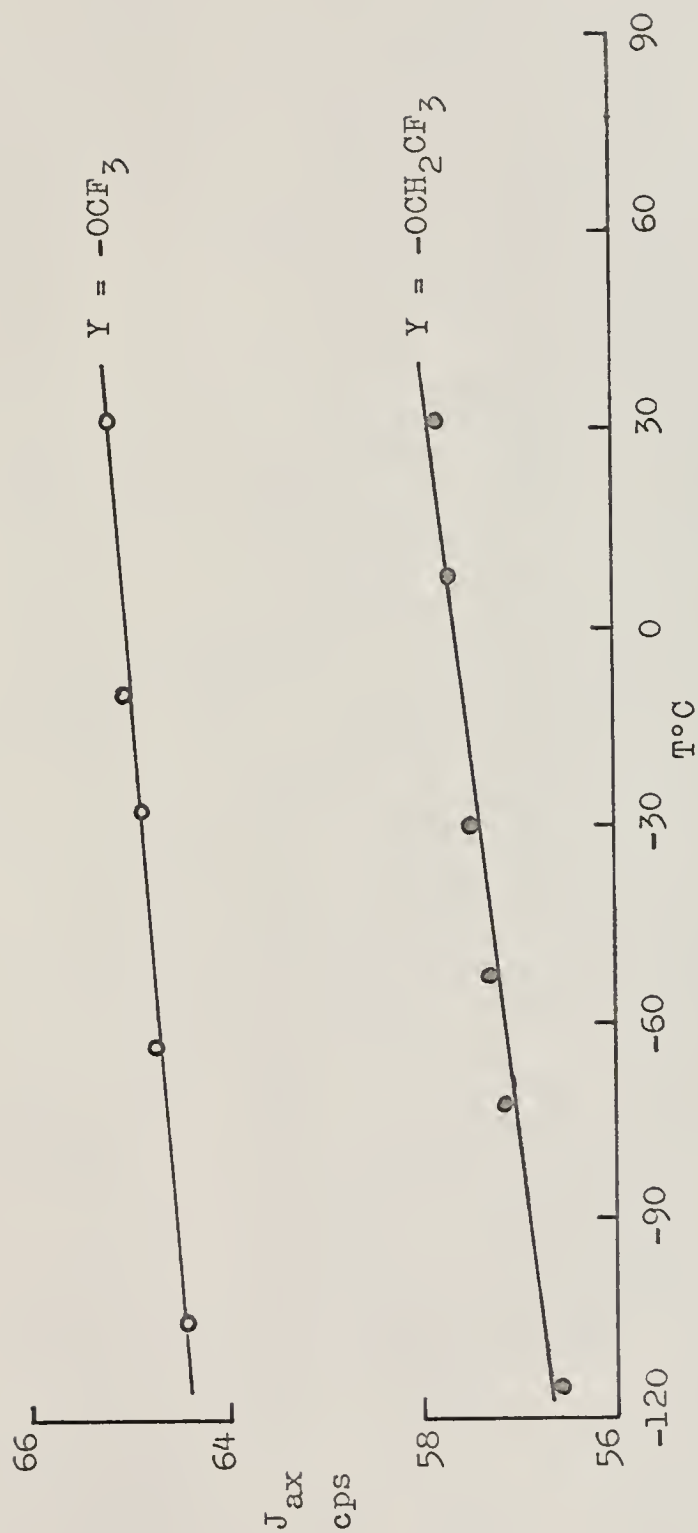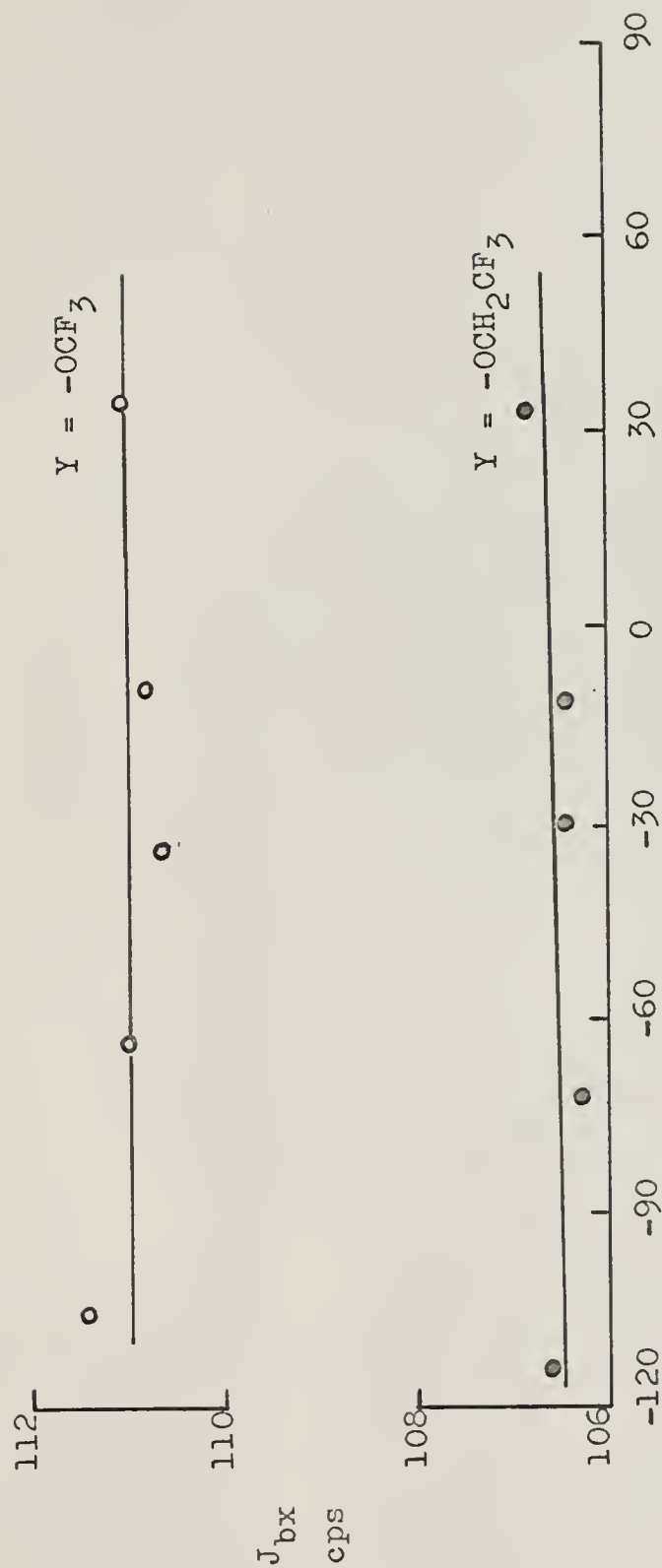
Fig. 11.—The temperature dependence of J_{bx} observed in some trifluoro-vinyl compounds of group II.
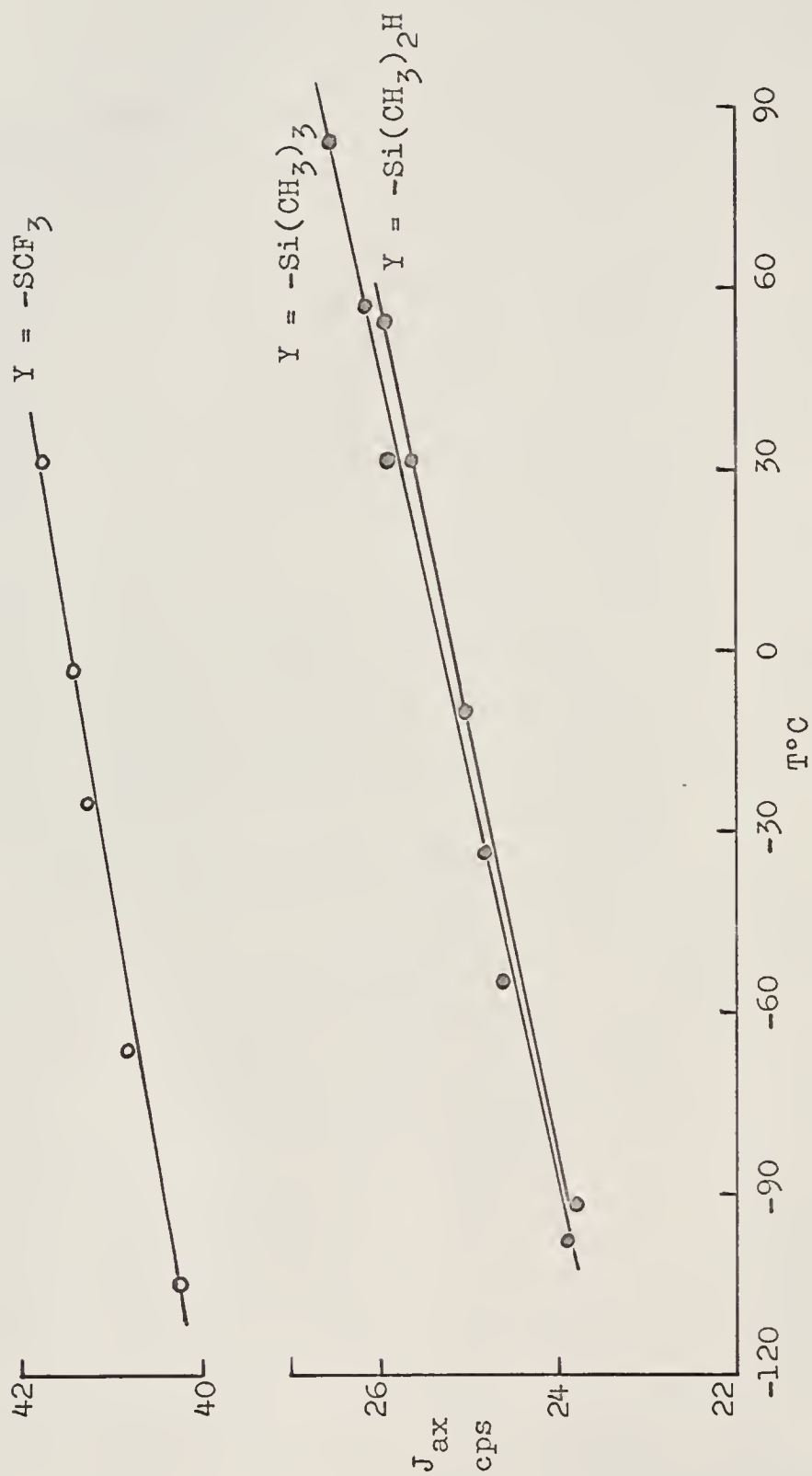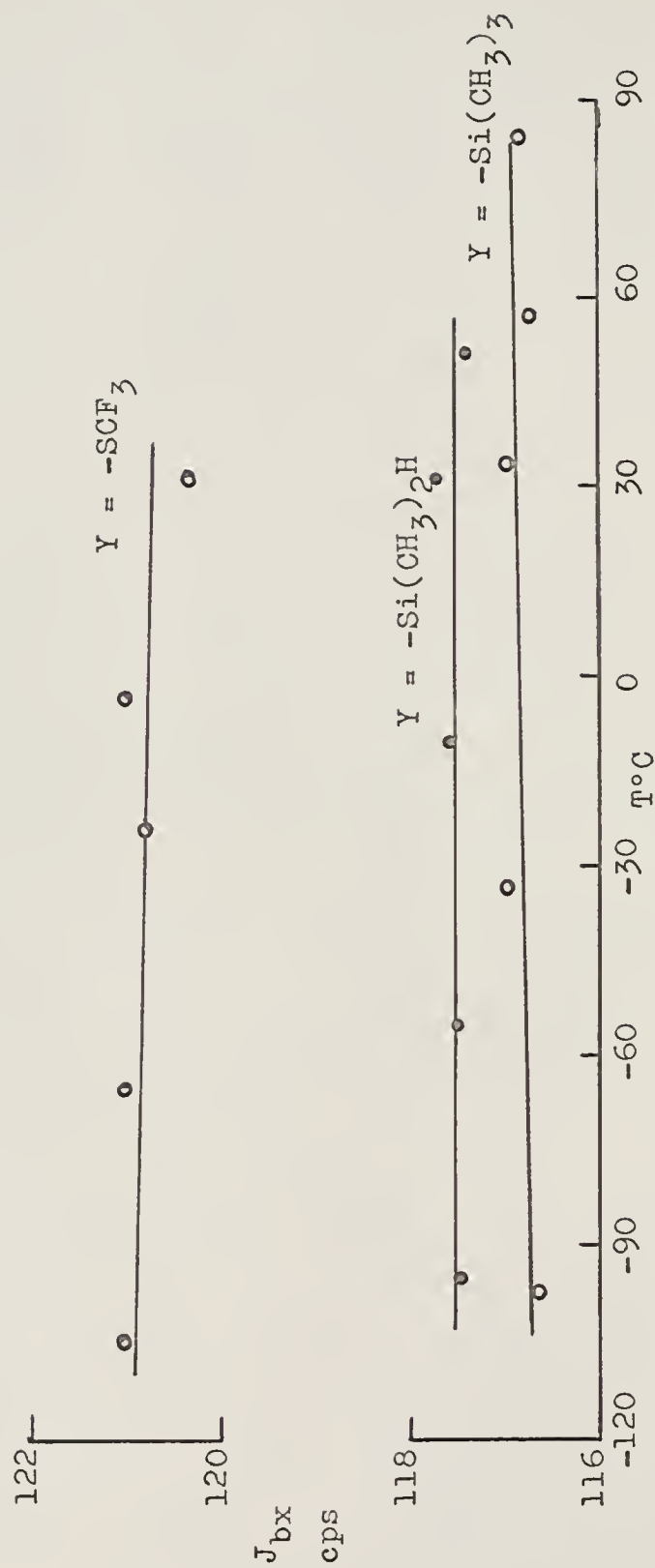
Fig. 12.—The temperature dependence of J_{bx} observed in some trifluoro-
vinyl compounds of group III.

DISCUSSION

The results of greatest importance in this work are:
1) the extreme sensitivity of the geminal coupling constants,
J_{ab}, and the chemical shifts of F_a to the conjugating ability
of the substituent, -Y; 2) the dependence of the cis coupling
constants, J_{ax}, and the chemical shifts of F_x on the electro-
negativity of the substituent atom which is directly attached
to the trifluorovinyl group, and 3) the temperature depen-
dence of the coupling constants J_{ab} and J_{ax}.

The trans coupling constants, J_{bx}, appear to be
insensitive to both the nature of the substituent and the
temperature. The chemical shifts of F_b do not correlate
with any specific property of the substituents.

Effect of Conjugation on J_{ab} and the Chemical Shifts of F_a

From an analysis of the chemical differences among
the substituents and from the values of the chemical shift
for F_a, it is possible to divide the compounds into three
main groups, as listed in Tables 1 and 2. In Group I,
there are seven compounds, each of which has a substituent
group that would not be expected to enter into conjugation
with the trifluorovinyl group. The values of the chemical

42

shift for F_a of these compounds range from 23 ppm to 30.4 ppm. The corresponding values for J_{ab} range from 78 cps to 92.5 cps.

In Group II, there are two compounds, $CF_2=CFOCF_3$ and $CF_2=CFOCH_2CF_3$. Both of these compounds have a substituent group which could enter into conjugation by contributing electrons to the trifluorovinyl group. Such a mechanism should increase the electron density at F_a over that of the compounds in Group I. This point is supported by the fact that the chemical shift values for F_a in these two compounds are 10 ppm to 23 ppm higher than the values for the compounds in Group I. Another point of importance is the fact that the chemical shift value for F_a in $CF_2=CFOCH_2CF_3$ is about 6 ppm higher than that in $CF_2=CFOCF_3$. As would be expected, the separation of the oxygen from the highly electronegative trifluoromethyl group by a methylene group has facilitated the ability of the oxygen to donate electrons. The values for J_{ab} are 87.5 cps and 101.6 cps, the higher value belonging to $CF_2=CFOCH_2CF_3$.

In Group III there are 13 compounds, each of which has a substituent group which could enter into conjugation by withdrawing electrons from the trifluorovinyl group. Such a mechanism should decrease the electron density at F_a in the compounds of Group I. This decrease should, of course, be more pronounced in comparison to the compounds of

Group II. Both of these points are supported by the fact that chemical shift values for F_a in the compounds of Group III are 7 to 37 ppm lower than those of Group I, and 21 to 53 ppm lower than those of Group II.

The above proposal that the different substituents in Group III are capable of withdrawing electrons from the trifluorovinyl group can be rationalized as follows: 1) the ability of sulfur, iodine and silicon (46) to withdraw π electrons from an unsaturated system to which they are bonded by utilizing vacant d orbitals, 2) the ability of the highly electronegative groups, $-CF_3$, $-CF_2Cl$, and $-CF_2Br$ to participate in double bond-no bond resonance (47), 3) the ability of B to accept π electrons into its vacant 2p orbital and 4) 1,3 conjugation in $CF_2=CFCOF$ and $CF_2=CFCN$.

Of the compounds listed in Table 2, $CF_2=CFCOF$ has the second lowest chemical shift value for F_a, 0.6 ppm, and the second lowest J_{ab} value, 6.0 cps. In comparison to the other compounds of Group III, this compound should, therefore, be highly conjugated. This prediction is verified by the fact that there are two NMR-distinguishable isomers at 105°C, because of restricted rotation about the central bond of the conjugated system (48).

The effect of conjugation on J_{ab} seems to be related to the electron density at F_a, since, as shown in Figure 1, the coupling constants J_{ab} increase regularly with an

increase in the value of the chemical shift of F_a. One possibility is that a decrease in electron density at F_a may cause an increase in the F_a-C-F_b bond angle, thereby producing a decrease in J_{ab} (assumed to be positive), if the coupling operates through the bond in the same way as for H-H geminal coupling (15) and/or if the coupling operates by a "through-space" mechanism similar to that proposed by Sederholm (22,26). Therefore, if this is the case, no specific proposal can be made concerning the mechanism of the coupling, but it would mean that compounds in Group III probably have larger values for the F_a-C-F_b bond angle than compounds in Group I or Group II and that within Group III, the more highly conjugated compounds probably have the larger values for the F_a-C-F_b bond angle. However, if J_{ab} is assumed to be negative, then an increase in the F_a-C-F_b bond angle causes an increase in the magnitude of J_{ab}; where, in this instance, an increase in magnitude is the same as an algebraic decrease in J_{ab}. This increase in J_{ab} with increasing angle would lead one to believe that the coupling operates almost solely by a "through-bond" mechanism similar to that in H-H geminal coupling (15), since an increase in the F_a-C-F_b bond angle should result in a decrease in J_{ab} if coupling operates by a "through-space" mechanism (22,26). Also, based upon the above hypothesis, the order of values for the F_a-C-F_b bond angle for the

various compounds would be reversed from that proposed above.

Another possibility is that a decrease in electron density at F_a may cause a decrease in the F_a—C—F_b angle. This assumption would lead to additional arguments concerning the F_a-F_b coupling mechanism depending again on whether J_{ab} is assumed to be negative or positive.

Still, another possibility is that a decrease in electron density at F_a may mean that some of the electrons that actually transmit the coupling information between F_a and F_b are being withdrawn. Such a proposal would lead one to believe that the geminal coupling operates almost solely by a "through-bond" mechanism. Also, this would lead one to believe that the σ electrons in the C-F_a bond are being withdrawn rather than the π electrons around F_a, since compounds of Groups II and III do conjugate, but with an opposite effect on J_{ab}.

Although the answer to this problem awaits further evidence, it can be stated with reasonable assurance that the chemical shift values for F_a and the values for J_{ab} are directly related to the degree of conjugation in trifluorovinyl derivatives of the type $F_aF_bC=CF_xY$.

Dependence of the Chemical Shifts of F_x and J_{ax} on
the Electronegativity of the Substituent Atoms

From a comparison of the different substituents with
the chemical shifts of F_x and the coupling constants, J_{ax},
it is possible to correlate both parameters with the
electronegativity of the substituent atom directly attached
to the trifluorovinyl group.

As pointed out in Table 3 and Figure 2, the shift
of the geminal fluorine F_x goes regularly to lower fields
in the series Si to O, with some 60 ppm difference between
the extremes. This trend is parallel to that found for
binary fluorides (3,4): The more electronegative the
attached atom, the greater the downfield shift. A similar
trend is found in the series CFH_3, CF_2H_2, CF_3H and CF_4,
where successive replacement of H atoms of methane by the
more electronegative F atom causes a progressive displace-
ment of the fluorine resonance to lower fields (5).

The downfield shift of F_x (a decrease in the values
of the chemical shift) means that F_x is magnetically un-
shielded as the electronegativity of the substituent atom
increases. This may mean that the electron density of F_x
is decreasing as the electron withdrawing power of the
substituent atom increases. It could also mean that the
covalent character of the C–F_x bond is increasing as the

electronegativity of the substituent atom increases, since, as pointed out by Saika and Slichter (2), the paramagnetic contribution to fluorine chemical shifts is largest for covalent bonds. An increase in the covalent character of the $C-F_x$ bond in this instance could be explained as follows: The more electronegative substituent atoms withdraw electrons from the vicinity of C, followed by back donation of electrons from F_x to C.

It is apparent from Figure 2, that the electronegativity of the substituent atom is not the sole factor which affects the chemical shifts of F_x. The most obvious discrepancy is found for substituent atoms C, S, I: All three atoms have a Pauling electronegativity value of 2.5, but corresponding chemical shift values for F_x of 108 ppm, 76.5 ppm, and 71.8 ppm. The difference might possibly be related to the fact that both S and I do enter into conjugation with the trifluorovinyl group and both have unshared pairs of electrons. This abundance of electrons in the vicinity of the atoms could possibly produce a magnetization at F_x which is in the same direction as the magnetic field. This same effect might also be operative in the cases of Cl and O, in which case the chemical shift values for F_x are probably lower than what one would expect solely on the basis of electronegativity.

As shown in Table 3 and Figure 4, the values for the cis coupling constants, J_{ax}, increase with an increase in the electronegativity of the substituent atoms. In comparison to the trend observed for the chemical shifts of F_x this could imply that J_{ax} increases as the electron density at F_x decreases. This is in direct contradiction to what one would predict. However, if one assumes that increased covalent character of the $C-F_x$ bond accounts for the increase in the chemical shifts of F_x, then the increase in the values of J_{ax} with electronegativity could be rationalized as follows: As electrons are more evenly distributed between C and F_x it would facilitate the through-bond coupling mechanism in the system $F_a-C=C-F_x$. Although the cis coupling constants, J_{ax}, seem clearly to be related to the electronegativity of the substituent atom, it does seem that there are other, less obvious, factors which affect J_{ax}. This observation is based upon the fact that the values of J_{ax} are 35.3 cps, 41.7 cps, and 52.2 cps for C, S, and I, respectively; all have a Pauling electronegativity value of 2.5. Since both S and I have unshared pairs of electrons and both enter into conjugation with the trifluorovinyl group, may in some way explain why they are not more in line with C. Either or both of these effects may also contribute to J_{ax} in the other compounds.

Temperature Dependence of the Coupling Constants J_{ab} and J_{ax}

The geminal coupling constants, J_{ab}, and the cis coupling constants, J_{ax}, increase with increasing temperature, as shown in Figures 4 through 6 and Figures 7 through 9, respectively. This change in coupling constants is small in both cases, but significant.

The cis coupling constants, J_{ax}, increased about 1.0 to 2.0 cps for a 150°C temperature rise; the change does not appear to be related to the conjugation or electronegativity effects cited earlier.

The geminal coupling constants, J_{ab}, increased about 0.5 to 2.0 cps for a 150°C temperature rise. For compounds of Group I, this increase in J_{ax} is approximately 0.5 cps, while for compounds of Group II and Group III, this increase is about 1.0 cps. Since Group I compounds have substituent groups which would not be expected to conjugate with the trifluorovinyl group and Groups II and III compounds do, might lead one to believe that the temperature dependence of J_{ax} is somehow related to the temperature dependence of conjugation (i.e., the fact that conjugation usually increases with decreasing temperature). However, if one recalls that values for J_{ax} decrease with conjugation for Group III compounds and increase with conjugation for Group II compounds, then it would not seem likely that the temperature dependence of J_{ax} is related to any conjugation effect.

Recently Ramey and Brey (43) have reported on the temperature dependence of spin-spin coupling constants of fluoropropenes of the type $F_aF_bC = CF_xY$, where $Y = CF_3$, CF_2Cl, CF_2Br, and CF_2Br. Since, as postulated above, the temperature dependence of J_{ab} and J_{ax} does not appear to be related to any substituent effects, it seems likely that the arguments advanced by them can be generalized to apply to any of the trifluorovinyl derivatives studied here. They postulated that the explanation for the increase in the values for J_{ab} and J_{ax} with increasing temperatures may lie in the greater excitation, with increasing temperature, of molecular vibrations. By assuming that the CF_2 deformation would have the most influence on the temperature dependence of J_{ab}, they were able to show, by use of the Boltzmann distribution, that the fraction of molecules in excited states for this mode is 0.05 at $-100°$ and 0.26 at $+100°$. This significant change in population coupled with the fact that, for the ground state, the system spends the larger amount of time near the equilibrium configuration, while for excited states, it spends most of the time near the extremes of the vibration, lead them to propose possible mechanisms for F_a-F_b coupling consistent with the observed increase in J_{ab} with temperature. They proposed that if the symmetric in-plane deformation of the geminal fluorines is

strongly anharmonic, then: 1) J_{ab} should be expected to increase sharply as the atoms approach one another, if there is a through-space contribution to the coupling constant, and 2) J_{ab} should again be expected to increase with decreasing angle if a through-bond contribution to J_{ab} operates in the same way as for the H-H geminal coupling.

These possibilities were, of course, not meant to be interpreted as the absolute solution to the problem of geminal fluorine-fluorine coupling. There is always the possibility that the two contributions may operate simultaneously. Any other possibility would also have to take into account the symmetry or asymmetry of the potential well for the symmetric in-plane deformation of the CF_2 group and the relation of J_{ab} to the position of the atoms, F_a and F_b.

Although it is not possible to make any specific prediction concerning the mechanisms of the fluorine-fluorine coupling, it does, however, seem likely that the temperature dependence of J_{ab} and J_{ax} is related to vibrational excitation in the trifluorovinyl derivatives.

SUMMARY

A variety of trifluorovinyl derivatives of the type $F_aF_bC = CF_xY$ have been examined and the following correlations have been drawn between the observed NMR parameters and the substituent, Y: 1) F_a chemical shifts and J_{ab} coupling constants depend on the conjugating ability of Y, 2) F_x chemical shifts and J_{ax} coupling constants depend on the electronegativity of the directly attached substituent atom, and 3) F_b chemical shifts and J_{bx} coupling constants are not related to any specific property of the substituent.

The temperature dependence of the spin-spin couplings, J_{ab} and J_{ax}, has been attributed to the excitation of vibrational modes in the molecules and has been found to be independent of the nature of the substituent.

Both the temperature dependence and the substituent dependence of the coupling constants, J_{ab}, have led to many alternative explanations which might shed some light on the mechanism of $F^{19} - F^{19}$ geminal coupling constants. As yet, no definite conclusions have been reached, but it is felt that the geminal coupling does probably proceed by the "through-space" and "through-bond" mechanisms, simultaneously.

Also, no definite conclusions have been reached concerning the molecular geometry of the trifluorovinyl group, but additional theoretical work on the mechanism of $F^{19} - F^{19}$ geminal coupling would probably make it possible to make some good predictions concerning the value of F_a-C-F_b bond angle.

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BIOGRAPHICAL SKETCH

Charles Glen Moreland, Jr. was born November 24, 1936, at St. Petersburg, Florida. In June, 1955, he was graduated from St. Petersburg High School. In June, 1957, he received the degree of Associate of Arts from St. Petersburg Junior College, and in February, 1960, he received, with honors, the degree of Bachelor of Science in Chemistry from the University of Florida.

In February, 1960, Mr. Moreland entered the Graduate School of the University of Florida. He worked as a research assistant in the Department of Chemistry until September, 1960, when he received a National Defense Act Fellowship. He received the degree of Master of Science with a major in Chemistry in June, 1962. From June, 1962, until the present time he has pursued his work toward the degree of Doctor of Philosophy with a major in Chemistry.

Charles Glen Moreland is married to the former Nancy Louise Park and has one son, John Calloway. He is a member of the American Chemical Society and Phi Beta Kappa Honorary Fraternity.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 8, 1964

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Dean, College of Arts and Sciences

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Dean, Graduate School

Supervisory Committee:

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Chairman

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